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Characterization of unextractable organic matter associated with heavy minerals from oil sand*

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Considerable quantities of organic matter are associated with heavy metal minerals recovered from Suncor aqueous sludge. This organic matter is not extractable with common organic solvents. Attempts were made to concentrate this organic matter by dissolving the mineral matter in acids. Various soluble fractions were also obtained by extraction with methanol/benzene (1:4) after each dissolution step. All these fractions were analysed by elemental analysis, infrared, proton and ^{13}C nuclear magnetic resonance spectroscopy.

(Keywords: oil sand; humic acids; structural analysis)

Athabasca oil sand is a complex, variable mixture of bitumen, sand, water and clays¹. The total reserves of oil sand deposits are estimated to contain close to $2.15 \times 10^{11} \text{ m}^3$ of bitumen in place²⁻⁵. The largest deposit alone, in the Athabasca area, contains over $1.4 \times 10^{11} \text{ m}^3$ of bitumen. The Athabasca deposit is also the only one currently under commercial exploitation, by Suncor and Syncrude using the hot water extraction process pioneered and developed in the 1920s by Clark⁶. This process results in very large volumes of tailings, consisting mainly of sand and a dispersion of various clays containing residual organic matter^{1,7-9}. The sand settles rapidly from the tailings and presents no real disposal problem. It is in fact used to build containment dikes for aqueous sludges that show little tendency to dewater, even when subjected to mechanical dewatering procedures¹⁰. It is the buildup of these partially settled clay sludges, or slimes, necessarily contained behind the sand dikes, which present not only an environmental problem but also a significant repository for non-recycleable water.

The reason for the intractability of the clay slimes has been a subject of considerable study^{1,7,9,11-13}. Considerable quantities of insoluble organic material are known to be associated with these clay slimes^{8,14,15}, as well as residual bitumen. Most of this organic material is strongly associated with the mineral fines and is not soluble in the common organic solvents under mild conditions¹⁶.

Based on the results of the published work it is generally believed that the interaction of organics with clay minerals is important in determining the nature of the oil sand slimes^{8,14,15}. The interaction is thought to provide a hydrophobic character to the clay particle surfaces allowing bridging through residual bitumen to set up a weak gel structure.

Relatively little information is currently available concerning the association between organic matter and

the minerals phase in oil sands. The authors have recently developed a technique for concentrating unextractable, residual organic matter from oil sand tailings⁸. The objective of this study was to further characterize the nature of this organic matter, and the nature of the bonding between these oil sand constituents. This information may also be of use in understanding the formation of oil sand deposits and perhaps provide insight into beneficiation and enrichment of the organic matter in low grade oil sands that are known to contain significant quantities of unextractable organic matter¹⁶.

Organic concentrate obtained from oil sand tailings was preferentially separated in a series of acid treatments (HCl, HF) to remove minerals, followed by the removal of bitumen by a Soxhlet extraction method using benzene/methanol. It is well known that HCl dissolved most carbonates and that pure HF or HF/HCl mixtures effectively remove silicates, quartz and clay minerals^{17,18}. The various fractions thus isolated were studied using elemental analyses and spectroscopic techniques. The data are discussed in terms of the chemical structure of this residual organic matter and the nature of bonding between the mineral phase and the organic phase of oil sands.

EXPERIMENTAL

Aqueous tailings in 5 gallon to barrel-size lots were obtained from the Suncor plant sludge pond, and contained 5–12% solids by weight, although in some lots the solids content ranged as high as 30%.

Concentration of oil phase solids

The general procedure for isolating various fractions from Suncor sludge is shown in *Figure 1*. A counter-current stirring device (grease kettle)¹⁹ was used to collect emulsified bitumen from the heavy sludge. An oleaginous phase, amounting to 10–12% by weight of the original sludge, was collected on the stirring vanes with the grease kettle cooled in an ice bath. While stirring, the 'oil' was washed several times with water at pH 10 in order to

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Figure 1 Flowsheet for the fractionation of aqueous sludge

remove occluded water-dispersible finely divided mineral particles. Bitumen was extracted from the oil phase with toluene, leaving a residue in the form of a water repellent, dark powder 'oil phase solids', amounting to 2–4% by weight of the original sludge. Based on the loss on ignition at 400°C²⁰ of oil phase solids, 20–30% of organic matter was estimated to be associated with this fraction. The inorganic portion of the oil phase solids (OPS) consisted mainly of heavy metal minerals of titanium, iron, zirconium, aluminium, calcium, magnesium and manganese. A typical analysis of an OPS sample is given in Table 1.

Attempts were made to isolate the organic matter from oil phase solids using various solvents and mixtures of solvents. This only removed small quantities of this material leaving the major portion insoluble. Some of the more polar solvents like pyridine, methanol, THF and DMSO were found to be adsorbed strongly during extraction.

Separation of bitumen fractions and kerogen

In order to isolate the organic matter from the oil phase solids, the inorganic matter was selectively dissolved in various acids^{21,22}. The general procedure for mineral dissolution and bitumen extraction is presented in Figure 2, which also shows material balance for each step.

In general, after extraction by refluxing with methanol/benzene (1:4), the suspension was centrifuged and the liquid phase decanted. The solid material was then stirred with fresh methanol/benzene (1:4), centrifuged and decanted, until the rinse solutions were colourless or nearly so. The decanted liquid was filtered on Whatman GF/F glass filter (98% retention of particles > 0.7 µm) and the solvent removed by a rotovaporator (Brinkman) at 100°C under reduced pressure. The bitumen was further dried at 70°C under vacuum for 18 h.

The remaining mineral matter was similarly dried before further processing.

Before treatment with acid the solid fractions of the oil phase solids were wetted with methyl alcohol (to improve wetting of the solid and acid). Acid solutions were first added dropwise to control gas and heat evolution and then the suspensions were stirred for 36–48 h. Hydrofluoric acid treatments were performed in vessels made of polyethylene or Teflon. Insoluble fluoride salts were converted to more soluble forms by stirring warm saturated boric acid solution with the oil phase solids residue for 4–6 h after its treatment with HF and HCl/HF.

Elemental analysis

C, H and N analyses were performed using a Perkin–Elmer model 240 CHN analyser. Carbonate carbon was measured titrimetrically after acid digestion. Organic carbon was then determined by subtracting carbonate

Table 1 Analytical data for a typical oil phase solid sample

	Wt %
Loss of ignition at 380°C	32.5
Carbon	19.3
Hydrogen	1.4
Nitrogen	0.3
Sulphur	3.5
SiO ₂	13.0
Al ₂ O ₃	5.0
Ti	18.0
Zr	2.0
Fe	8.6
Cu	0.05
Ni	0.03
Mn	0.21
Zn	0.04

Figure 2 Flowsheet for the treatment of oil phase solids by successive acid leaching and extraction of bitumen by 1:4 (methanol:benzene)

carbon from total carbon. Sulphur was analysed as total sulphur using X-ray fluorescence spectroscopy. Oxygen was determined either by difference or directly²³. For mineral samples containing adsorbed organic matter, the ultimate analysis was done at the Energy Mines and Resources laboratory using ASTM procedure D271.

Ash content

Ash content of oil phase solids and their solid fractions was determined by heating at $380 \pm 10^\circ\text{C}$ to constant weight. After cooling to room temperature, the samples were soaked in water for 4 h and finally dried at 110°C to constant weight. The difference between the initial and the final weights was taken as 'loss on ignition'²⁰.

Instrumental analysis

Infrared spectra were recorded using a Perkin-Elmer model 683 i.r. spectrometer. Solid and insoluble samples were run as KBr pellets while most of the bitumen samples were run either as solutions in CCl_4 or CH_2Cl_2 or thin films on KBr or NaCl plates. The films were formed either by pressing a drop between the plates or evaporating the solvent from the solution placed on the plates. Because of the poor solubilities of most of the fractions, quantitative studies were not feasible. The spectra were therefore used only qualitatively, for quick identification of general features and the presence or absence of functional groups.

Proton n.m.r. measurements were performed on a Varian EM-360 n.m.r. spectrometer (60 MHz), except for a few samples which were run on a Bruker CXP180 n.m.r. spectrometer. Spectra were recorded in solution in CCl_4 , CDCl_3 , CH_2Cl_2 or deuteropyridine. The solutions were filtered using an n.m.r. sample filtering device (Wilmad Cat. No. 807 and 808) before recording the spectra.

All solid state ^{13}C n.m.r. spectra were obtained at 22.6 MHz on a Bruker CXP180/90 n.m.r. spectrometer using the cross polarization (CP) technique with magic angle spinning (MAS). A contact time of 1 ms and a repetition time of 2 s were selected. The magic angle spinning speeds were 3.0–3.4 KHz. Chemical shifts were determined by substitution relative to tetramethylsilane (TMS). Each spectrum was the Fourier transform of 3000–10 000 free-induction decay curves. The dipolar dephasing technique²⁴ was used for Kerogen D to distinguish the non protonated carbons (except groups in motion, e.g. CH_3) from those attached to hydrogens.

^{13}C spectra of soluble fractions were run as saturated solutions in CDCl_3 , employing proton decoupling and 10 000–20 000 pulses at intervals of 2 s.

RESULTS AND DISCUSSION

Concentration of organic matter from OPS

There is no satisfactory method for the determination of the elemental composition of the organic matter associated with inorganic or mineral matter²¹. This is because of the contribution of inorganic or mineral components to the organic elemental analyses. For such systems the determinations of the elemental compositions, particularly with combustion techniques, reflects total rather than organic analyses. The best route for determining the average composition of the organic matter in such systems is to remove as much of the inorganic material as possible, leaving a kerogen

concentrate²². Such a scheme was adopted for the concentration of organic matter from oil phase solids. The inorganic component of the oil phase solids was dissolved in acids as shown in Figure 2. After each treatment, soluble fractions were extracted using methanol/benzene (1:4). As is evident from the mass balances, acid leaching released $\approx 8\%$ more bitumen than could be extracted without acid treatment. It appears that some bitumen was trapped inside the minerals and is not released until some of the mineral is dissolved. There is also a possibility of the chemical reaction of the organic matter during acid treatments, rendering some of the material soluble. Possibly, both of these factors contribute to the release of additional organic matter.

Acid dissolution schemes employed for the concentration of organic matter from oil phase solids modify this organic matter by incorporation of halogens. Although this is undesirable, under the circumstances it is the best method to reduce the ash content of oil phase solids. A major portion of the heavy elements dissolve in acids, suggesting the presence of heavy metal soaps with bitumen acids. Considerable amounts of acids and bases capable of salt formation are known to be present in bitumen²⁵. Heavy elements present in oil sands are concentrated in froth during hot water processing of oil sands. This provides ideal conditions for salt formation between heavy metal oxides and acidic and basic components of bitumen.

Elemental analyses

Elemental analyses of oil phase solids and their fractions were obtained using standard methods. Carbon analyses were corrected for carbonate carbon to determine true organic carbon. No corrections were applied for hydrogen, nitrogen and sulphur analyses. These analyses thus reflect total rather than organic analysis. There is no satisfactory method for the direct determination of oxygen from the organic matter associated with mineral matter²². Applications of the standard difference method may lead to large errors because of the high mineral content of the oil phase solids and its solid fractions. Oxygen contents by direct determinations²³ and by difference were found to be similar. However, the accuracy is limited by the possibility of errors in each method.

The elemental compositions of bitumen, asphaltenes, maltenes and the benzene/methanol soluble fractions obtained from oil phase solids are reported in Table 2. Examination of the data leads to the following conclusions:

1. The nitrogen and oxygen content of the benzene/methanol soluble fractions and humic acid and fulvic acid fractions is substantially higher than reported for bitumen and heavy oil fractions in the literature.
2. Oxygen is the most abundant heteroatom in the benzene/methanol soluble fractions including humic acid and fulvic acid fractions.
3. The carbon content of these fractions is considerably lower than that of the corresponding asphaltenes, maltenes and bitumen of the bituminous sand feedstock.
4. The hydrogen content of the benzene/methanol soluble fractions appears to be in the same range as for the asphaltenes.

Table 2 Elemental analysis of soluble fractions of adsorbed organic matter from oil sand tailings (in percentage of dry, ash free weight)

Sample ^a	Wt %					Atomic ratios			
	C	H	N	S	O ^b	H:C	N:C	S:C	O:C
A typical bitumen sample ^d	83.40	10.53	0.44	4.76	0.87	1.52	0.0045	0.021	0.008
Sludge pond bitumen	81.13	8.90	0.61	6.02	3.32	1.32	0.0065	0.028	0.031
Maltenes from sludge pond bitumen	82.98	10.80	0.62	3.89	1.71	1.56	0.0064	0.018	0.015
Asphaltenes from sludge pond bitumen	80.19	7.99	1.15	7.85	2.82	1.18	0.012	0.036	0.017
Bitumen A	72.42	8.15	1.25	4.61	13.57	1.35	0.015	0.024	0.14
Bitumen B	72.13	7.21	1.70	6.07	12.89	1.20	0.02	0.032	0.13
Bitumen C	70.51	8.32	0.59	4.42	16.16	1.42	0.007	0.024	0.17
Bitumen D	68.67	7.99	1.72	4.13	15.69 ^c	1.40	0.021	0.023	0.17
Humic acids	59.51	4.41	5.45	1.83	28.8 ^c	0.89	0.078	0.012	0.36

^aKey to the compound name is found in Figure 2^bBy difference^cExperimentally determined values^dDean Wallace, Final Report Bitumen Round Robin No. 2, Alberta Research Council 1983**Table 3** Elemental analysis of insoluble fractions of adsorbed organic matter from oil sand tailings (in percentage of dry, ash free weight)

Sample ^a	Wt %						Atomic ratios			
	C	H	N	S	O	Halogens ^b	H:C	N:C	S:C	O:C
OPC ^c	61.24	5.22	2.82	4.15	26.57	—	1.02	0.039	0.025	0.33
OPS-A	61.18	5.18	2.36	4.50	26.78 ^d	—	1.02	0.33	0.028	0.33
OPS-B	61.94	4.95	2.12	4.67	26.32	N.D.	0.96	0.029	0.028	0.32
OPS-C	60.35	5.15	2.22	4.40	27.88	N.D.	1.02	0.32	0.026	0.35
OPS-D	60.90	4.76	2.40	4.45	27.49	N.D.	0.94	0.034	0.027	0.34
Kerogen A	58.60	4.77	2.68	4.40	29.55	—	0.98	0.039	0.028	0.38
Kerogen B	57.93	3.58	1.77	4.27	32.45	—	0.74	0.026	0.028	0.42
Kerogen C	55.66	3.16	1.84	4.35	21.0 ^d	13.28	0.68	0.028	0.029	0.28
Kerogen D	56.35	3.29	2.03	4.47	20.9 ^d	12.96	0.70	0.031	0.03	0.28

^aKey to the compound name is found in Figure 2^bTotal of all halogens^cOil phase solids. Heavy minerals fraction from oil sand tailings containing adsorbed organic matter^dExperimentally determined values; all other values determined by difference

N.D. = not determined

5. The sulphur content of the organic matter extracted from oil phase solids is in the same range as for the bitumen fractions of the feedstock.

The high content of heteroatoms (O and N) in organic matter associated with heavy metal minerals compared with that of the bitumen and asphaltenes of the bituminous sand feedstock suggests a stronger concentration of heterocyclic compounds in the former compared with the latter. Relatively large proportions of oxygen functions in the organic matter associated with oil phase solids would make it more hydrophilic thus contributing to emulsion formation and subsequent stability of sludge.

Hydrogen to carbon ratios of the benzene/methanol soluble fractions from oil phase solids are within the range of the bitumens and asphaltenes. However, the oxygen content is much higher than those for bitumens and asphaltenes of the bituminous sand feedstock. This suggests that the soluble organic matter extracted from oil phase solids after acid treatments is not simply the occluded organic matter. It is possible that some smaller oxygenated species like esters are produced during the course of reaction with acids, sodium hydroxide and methanol. On the other hand, it is possible that oxygenated species such as phenols and carboxylic acids are the main constituents of the organic matter associated with heavy metal minerals. Such compounds are known to form water soluble and water insoluble complexes with metal ions and hydrous oxides and interact with clay

minerals and hydrophobic organic compounds²⁶⁻²⁸. This will explain the lower carbon content of benzene/methanol soluble fractions compared with the bitumen fractions of the feedstock.

Elemental analyses of the organic matter associated with the solid fractions of the oil phase solids are listed in Table 3. All the fractions contain considerable quantities of heteroatoms, N, S and O. The sulphur content of the organic matter associated with oil phase solids and the bitumen fractions of bituminous sand feedstock all appear to be in the same range suggesting a more uniform distribution of sulphur compounds in bitumens. However, nitrogen and oxygen content of the organic matter associated with oil phase solids is considerably higher compared with the bitumen fractions of the feedstock bituminous sand. Higher oxygen content of this organic matter could be due, at least in part, to the retention of methanol because of adsorption on the mineral matter during extraction with benzene/methanol. There is also a strong possibility of this organic matter being humic matter which is a precursor to bitumen. This will also explain its higher heteroatom content.

The hydrogen:carbon ratio for the benzene/methanol insoluble organic matter associated with the oil phase solids, decreases gradually from ≈ 1.0 in the first four fractions to ≈ 0.7 in the last two fractions as the soluble organic matter is removed. This suggests higher paraffinic and naphthenic content of the benzene/methanol soluble fractions and consequently higher aromaticity of the insoluble fractions.

Analysis of kerogen C and kerogen D indicates considerable quantities of halogens. This suggests the interaction of conc. HCl and HF with the organic matter associated with oil phase solids after treatment with conc. HCl/HF. It is well established that certain organic compounds react readily with both hydrochloric and hydrofluoric acids to alter chemical/physical properties. For example, esters, amides, olefines, quinones and alcohols undergo various hydrolysis, addition, and alkyl halide formation reactions in the presence of HCl²⁹⁻³¹. In the case of HF, condensation reactions involving olefins and aromatic compounds occur readily³¹. Therefore, the attack of HCl and HF on the adsorbed organic matter in oil sands is not surprising.

Table 4 lists the elemental composition of solvent extracts from unmodified oil phase solids. Complete removal of the residual solvent from these fractions is very difficult. Retention of some solvent appears to have occurred for the pyridine extract, which has the highest nitrogen content of all the extracts. Distribution of the heteroatoms among various fractions does not follow any particular trend. Ethyl methyl ketone extract has the minimum nitrogen content followed by methylene chloride extract, whereas the nitrogen content of chloroform, methanol and THF extracts is in the same range. Sulphur containing components of the organic matter associated with heavy metal minerals appears to be least soluble in chloroform, followed by pyridine and ethyl methyl ketone extract. The sulphur content of methanol and methylene chloride extracts is in the same range as for the benzene/methanol soluble and insoluble organic matter from oil phase solids. However, the THF

extract appears to have the highest sulphur content. This preferential dissolution of sulphur containing components appears to be contrary to the results of acid dissolution studies that indicate a more uniform distribution of sulphur compounds.

Oxygen content of the extracts in Table 4 is higher than the feedstock bituminous sands bitumen fractions, but appears to be in the same range as for the fractions from acid dissolution scheme. Chloroform, methanol and ethyl methyl ketone extracts have the highest oxygen content whereas the methylene chloride extract has the lowest oxygen content.

Carbon and hydrogen content and the H:C ratio of the extracts in Table 4 appear to be in the same range as for the benzene/methanol solubles from oil phase solids. This suggests that the hydrocarbon portion of the two extracts is essentially similar. Heterocyclic components of the two extracts on the other hand appear to be significantly different as indicated from the heteroatom content (N,S,O) of the two extracts.

Table 5 lists the ultimate analyses of various organic materials that are thought to be the precursors of coals, kerogens and oils³². Comparison of the elemental compositions of the benzene/methanol insoluble organic material associated with oil phase solids with the composition of the materials in Table 5 suggests that the composition of the former is almost identical to those of peats and humic materials.

Elemental distributions

Total elemental content of various fractions from OPS is shown in Table 6. This is based on the 100 g of original

Table 4 Elemental composition of solvent extracts from oil phase solids^a

Sample	Wt %						Atomic ratios			
	Ash	C	H	N	S	O ^b	H:C	N:C	S:C	O:C
Chloroform extract	14.0	56.6	6.6	1.5	0.93	34.4	1.40	0.02	0.006	0.45
Methanol extract	1.8	55.3	7.10	1.1	5.2	31.3	1.53	0.02	0.035	0.43
Methylene chloride extract	—	71.4	8.8	0.8	5.5	13.5	1.47	0.01	0.03	0.14
THF extract	3.5	62.4	6.4	1.6	8.4	21.2	1.24	0.02	0.05	0.25
Pyridine extract	5.6	68.8	6.3	3.3	2.5	19.1	1.10	0.04	0.01	0.21
Ethyl methyl ketone extract	13.8	59.2	6.8	0.2	2.5	31.3	1.39	0.003	0.016	0.395

^aIn percentage of dry, ash free weight

^bBy difference

Table 5 Ultimate analyses of organic materials in the fossilization pathway (in percentage of dry, ash-free weight)^a

Sample	Wt %				Atomic ratios		
	C	H	N	O	H:C	N:C	O:C
Carbohydrate	44.0	6	—	49.0	1.64	—	0.84
Protein	58	7	11	23	1.45	0.16	0.297
Fat	75	12	—	12	1.92	—	0.12
Fulvic acids	47	4.4	2	46	1.12	0.04	0.73
Peats (recent)	53	6	1	38	1.36	0.02	0.54
Humins	56	5.7	5	33	1.22	0.08	0.44
Humic acids	59	5	3	34	1.02	0.04	0.43
Peats (old)	59	6	2	31	1.22	0.03	0.39
Lignites	70	5	—	25	0.86	—	0.27
Coal mid-rank	85	5	1.5	8	0.71	0.015	0.07
Coals anthracite	92	4	—	2	0.52	—	0.016
Humic material from oil sands ^b	60.6	3.9	1.3	21.7	0.77	0.02	0.27

^aR. Hartenstein, *Science* 1981, **212**, 743

^bD. S. Montgomery, *Adv. Pet. recovery and upgrading*, Calgary, Alberta, 1981

Table 6 Total elemental concentrations^a

Sample ^b	Ash	C	H	N	S	Hal ^c	O ^d
OPS	79.68	12.56	1.26	0.68	2.76	—	6.41
OPS-A	(A) 80.50	12.23	1.12	0.51	2.80	—	7.10
Bitumen A	(B) —	1.44	0.17	0.02	0.09	—	0.34
A + B	80.50	13.67	1.29	0.53	2.89	—	7.44
OPS-B	(C) 72.90	11.51	0.96	0.41	2.61	—	(3.36)
Humic acid	(D) 0.02	0.91	0.07	0.08	0.03	—	(0.44)
Fulvic acids	(E) 3.95 ^e	0.30	0.06	0.02	0.11	—	(0.69)
C + D + E	76.87	12.72	1.09	0.51	2.86	—	(4.49)
OPS-C	68.74	10.92	0.93	0.72	2.55	—	(3.55)
OPS-D	(F) 68.60	11.01	0.93	0.47	2.55	—	(3.21)
Bitumen-B	(G) 0.01	0.45	0.05	0.01	0.04	—	(0.08)
F + G	68.61	11.46	0.98	0.48	2.59	—	(3.29)
Kerogen-A	53.98	11.05	0.76	0.31	2.60	—	(4.42)
Bitumen-C	(H) 0.05	1.25	0.15	0.01	0.08	—	(0.29)
Kerogen-B	(I) 48.97	9.85	0.64	0.37	2.73	—	(7.14)
H + I	49.02	11.10	0.79	0.38	2.81	—	(7.43)
Kerogen-C	9.40	10.99	0.62	0.36	1.00	2.62	4.15
Kerogen-D	(J) 9.45	10.21	0.56	0.35	0.99	—	3.58
Bitumen-D	(K) —	1.27	0.18	0.02	0.04	0.49	0.59
(J + K)	9.45	11.48	0.74	0.37	1.03	0.69	4.17
Total		15.83 (126.0%)	1.24 (98.4%)	0.51 (75.0%)	1.38 (50%)		

^aBased on the 100 gm of OPS^bKey for the sample name is found in Figure 2^cHalogens^dFrom direct determinations, values obtained by difference are given in parentheses^eIt was calculated as follows:

Total amounts of fulvic acids, dissolved silica and sodium chloride

Wt. of fulvic acids and silica obtained by subtracting the amounts of humic acid and OPS-B from the weight of OPS-A

Therefore the amount of NaCl

Total ash

True ash for fulvic acids and dissolved silica

= 7.15 gm

= 4.65 gm

= 7.15 - 4.65

= 2.50 gm

L.O.I.

= $\frac{100}{7.15}$ = $\frac{90.21}{100}$

= 6.45 gm

= Total ash - wt. of NaCl

= 6.45 - 2.5

= 3.95 gm

oil phase solids (OPS). Assuming no analytical errors, the total elemental content of all the fractions should add up to the elemental composition of OPS. Inspection of the data indicates a maximum discrepancy for carbon values. The total carbon adds up to 126% of the amount present in the OPS. This additional carbon could have resulted from the adsorption of solvent during extraction of the soluble matter at various stages, as is evident from the comparison of carbon contents of the fractions before and after extraction.

Carbon content of the soluble fractions accounts for 45% of the original carbon. However, considering the amount of adsorbed solvent, about 80% of the original carbon still remains insoluble.

Hydrogen content of the soluble fractions and the final concentrate from OPS (Kerogen-D) accounts for 98.4% of the hydrogen content of OPS. Approximately 54% of the original hydrogen appears with the soluble fractions. This is consistent with the greater aliphatic content of the soluble fractions compared with the insoluble fractions.

Nitrogen content of the soluble fractions accounts for only 23.5% of the amount present in OPS. 25% of the nitrogen is unaccounted for. This could be because of the loss of nitrogen associated with mineral matter or the attack of acids or alkalis to the organic nitrogen compounds giving off volatile or water soluble nitrogen compounds.

Sulphur compounds present in the organic matter associated with the heavy metals appear to be the most resistant to acid or alkali attack. Only 14% of the original sulphur appears in the soluble fractions. About 50% of the total sulphur present in oil phase solids is inorganic sulphur that dissolves on treatment with HCl/HF. This explains the loss of about 50% of sulphur during acid treatment.

Discrepancy in the halogen results is difficult to explain. Formation of volatile halogenated products during extraction with methanol/benzene or during the evaporation of solvent from bitumen-D could be one possibility.

Infrared spectra

The infrared spectra could provide some indication of the chemical nature of the material. I.r. enables one to detect the presence of chemical groups, preclude or limit the existence of proposed structures, and demonstrate similarities and differences in chemical structure of the organic materials studied. A composite infrared spectrum of a typical heavy mineral fraction containing adsorbed organic matter (oil phase solids) is shown in Figure 3a. The broad absorption band centred at 3440 cm^{-1} is attributed to O-H or N-H bonds; this interpretation has been reported for coal^{33,34} and coal asphaltenes³⁵. The absorption bands falling between 2850 and 2930 cm^{-1}

Figure 3 Infrared spectrum (KBr pellet) of (a) OPS, (b) Kerogen D

are due to naphthenic and/or aliphatic C–H vibrations. A broad and strong absorption centred at 1625 cm^{-1} could be attributed partly to a conjugated C=C bond and partly to carbonyl, the C=O group. A broad band at 1450 cm^{-1} and a strong and sharp band at 1390 cm^{-1} are due to bending frequencies of asymmetric C–CH₃ bond and/or methylene, and symmetric C–CH₃ bond, respectively. The group of bands located at 1180 , 1090 , 1030 and 910 cm^{-1} are closely related to the aromatic oxygenated compounds, such as aromatic ethers³³, and sulphoxides³⁶. The weak bands at 860 , 800 and 770 cm^{-1} are considered aromatic out of the plane frequencies and are important with regard to the nature of the structure of aromatic clusters.

Dissolution of the mineral matter improves the resolution of the bands in the infrared spectrum of the organic concentrate. This is demonstrated in Figure 3b, which is the infrared spectrum of the organic concentrate (kerogen D) obtained from OPS by dissolving mineral matter. A weak band at $\approx 3060\text{ cm}^{-1}$ assigned to aromatic C–H is now visible. Wiberley³⁷ has shown that the aromatic C–H band shifts to higher frequencies with decreasing ring number. Since the carbon–hydrogen absorption in the infrared spectrum of kerogen-D occurs at frequencies considerably higher than the $\approx 3030\text{ cm}^{-1}$ band found for asphaltenes, it is probable that the number of aromatic rings in kerogen-D is considerably lower than in the asphaltenes. This suggests that the organic matter associated with OPS might not be related to asphaltenes. Another significant change in the infrared spectrum of kerogen-D is the resolution of the 1625 cm^{-1} band into two distinct bands at 1715 and 1612 cm^{-1} . Hydrogen bonded ketones and/or quinones are known to absorb at $\approx 1600\text{ cm}^{-1}$ region³⁸. Based on this assignment, the band at 1610 cm^{-1} can be attributed partly to a conjugated C=C bond and partly to carbonyl C=O group of ketones and/or quinones. The band centred at 1715 cm^{-1} falls within the range of 1700 – 1760 cm^{-1} assigned to esters of polyfunctional phenols as well as to carboxylic acids^{39,40}. This suggests that a portion of the hydroxyl groups present in kerogen-D occur as collections of two or more hydroxyl functions on the same aromatic ring or on adjacent peripheral sites, or sites adjacent to a carbonyl function, in a condensed aromatic system. Another interesting feature of the infrared spectrum of kerogen-D is the change in the intensity of 1388 cm^{-1} band assigned to symmetric C–CH₃ bond. This band goes down in intensity to the extent that it is hardly visible in the infrared spectrum of the final

concentrate (kerogen-D), indicating reduced methyl content.

The infrared spectra of the soluble fractions from oil phase solids are shown in Figure 4a–d. Except for variations in the intensities of the various absorption bands, the spectra are essentially similar. The broad absorption band centred around $\approx 3300\text{ cm}^{-1}$ is attributed to O–H or N–H bonds. This band not only moves towards higher wavenumbers in the sequence from bitumen A to bitumen D, but also goes up in intensity. This means less hydrogen bonding and more OH or NH content of the latter fractions. Low intensity bands due to aromatic C–H stretching also move towards higher wavenumber for bitumen A to D suggesting decreasing ring number from bitumen A to D and thus a trend from asphaltenes to humic material. The two vibrations of the methyl group are located⁴¹ at 2950 and 2865 cm^{-1} , whereas the methylene band, which is the strongest, is located at 2920 cm^{-1} . Another methylene peak occurs at 2850 cm^{-1} . The broad band in the 2300 – 2800 cm^{-1} region could be assigned to the OH group of the polymeric carboxylic acids³⁶. The strong and broad band centred around 1730 cm^{-1} falls in the range for carboxylic acids or esters carbonyl bond⁴⁰.

The absorptions in the 1600 – 1700 cm^{-1} region for bitumen A and bitumen B are different from those for bitumen C and bitumen D. Bitumen A and bitumen B have two absorptions in this region centred at 1605 and 1660 cm^{-1} indicating the presence of a conjugated C=C bond and hydrogen bonded ketone and/or quinone⁴⁰. Bitumen C has a series of bands in the 1600 – 1700 cm^{-1} range. A weak band at 1590 cm^{-1} could be assigned to a conjugated C=C bond, whereas the three bands at 1600 , 1620 and 1640 cm^{-1} could be attributed to the carbonyl groups of quinone and/or ketones. Similar assignments can be made for bitumen D, which has a very broad band in this region. Two bands at 1375 and 1460 cm^{-1} are due to bending frequencies of (1) asymmetric C–CH₃ bond

Figure 4 Infrared spectra (KBr pellet) of the soluble fractions from OPS (a) bitumen A, (b) bitumen B, (c) bitumen C and (d) bitumen D; methylene chloride solution spectra in the 3500 – 3900 cm^{-1} region is shown in dotted lines

and/or methylene, and (2) symmetric C-CH₃ bond, respectively. The groups of bands in the region 1400–950 cm⁻¹ are attributed to S=O and C–O vibrations for aromatic oxygenated compounds and/or sulphonated compounds. Long wavelength bands in the 800–600 cm⁻¹ region are considered aromatic out of plane frequencies. These are quite strong in the bitumen C spectrum compared with others. This suggests higher aromatic content for bitumen C.

To confirm the hydrogen bonding in these compounds, the spectra were also obtained as dilute solution in methylene chloride (the samples were not soluble in CCl₄ or CHCl₃). These spectra are shown in Figures 4–5. The broad band at ≈3300 cm⁻¹ is now a sharp band at ≈3600 cm⁻¹ which is consistent with the assignment of this band to hydrogen bonded alcohols or phenols. The bands in the carbonyl region (1700–2000 cm⁻¹) are also resolved as is illustrated in Figures 5a–d.

Figure 6 shows the infrared spectrum of humic acid, water solubles and acetone-chloroform extract from OPS. The essential features of the humic acid spectrum are the same as of other fractions. The major difference in the spectrum of humic acid from those of the other fractions is the relative intensity of the various bands. The spectrum shows absorptions due to hydrogen bonded OH, C–H, carboxylic, quinone and/or ketone C=O, C–O and aromatic out of the plane vibrations.

The infrared spectrum of the water soluble component of oil phase solids is a typical spectrum of water soluble asphaltic acids extracted from tar sands⁴². It exhibits both the C–H absorptions at frequencies of 2850–3000 cm⁻¹ and 1350 to 1460 cm⁻¹, and absorptions at 3150–3600 cm⁻¹ and 1715 cm⁻¹ corresponding to hydrogen bonded hydroxyl and carbonyl groups of carboxylic acids respectively. Broad absorption in the region 1000–1150 cm⁻¹ is in the range where oxygenated sulphur groups are known to absorb⁴⁰.

Small quantities of organic material from oil phase solids were extracted using the polar solvents methanol, pyridine, dimethylsulphoxide, tetrahydrofuran, ethyl-methyl ketone, acetone–chloroform (50:50) mixture and methylene chloride. The infrared spectra of various solvent extracts were remarkably similar. The acetone–chloroform extract spectrum shown in Figure 6c is typical. Comparison of this spectrum with the spectra of the other fractions shows the presence of hydrogen bonded carboxylic acids and sulphonates from the bands in the regions 3300 cm⁻¹, 1715 cm⁻¹ and 1300–900 cm⁻¹. A moderate intensity absorption at 1600 cm⁻¹ indicates that the acids are partly aromatic in character.

Figure 6 Infrared spectrum of (a) humic acid obtained from OPS, (b) water solubles obtained from OPS, (c) acetone–chloroform extract from OPS

Proton n.m.r. spectra

Proton n.m.r. chemical shifts of various fractions recovered from oil phase solids are listed in Table 7 along with those of bitumen and asphaltenes for comparison. The bitumen recovered from Suncor sludge had a slightly different spectrum compared with that of the bitumen extracted from fresh oil sands. Whereas the aromatic protons appear as a single broad peak in the spectrum of the bitumen from bituminous feedstock, two well defined regions are apparent in the spectrum of sludge pond bitumens. Not only was the polyaromatic region well defined for the sludge pond bitumen, its total aromatic content was also higher compared with the bitumen from bituminous feedstock. This is consistent with the higher asphaltene content of the sludge pond bitumen.

One of the common features of all the proton n.m.r. spectra of the fractions recovered from oil phase solids is a band at ≈3.6 ppm. This band is not observed in the spectra of bitumens or asphaltenes. It could be either assigned to residual methanol (chemical shift 3.35 ppm) or bridge methylene groups⁴³. Assignment of this peak to residual methanol alone cannot be justified because of the two reasons. Firstly, this signal is also present in the methylene chloride extract in which case the oil phase solids were not treated with methanol. Secondly, the solvent was evaporated under similar conditions from each fraction. If the peak at 3.6 ppm were due to residual solvent, its intensity would have been comparable. However, as is evident from Figures 7 and 8 the intensity of this peak varies considerably. It is still possible that a small amount of methanol is associated with these fractions, e.g. through hydrogen bonding, and hence cannot be removed completely. This fact along with the

Figure 5 Infrared spectrum of the soluble fractions from OPS in the region 1500–2000 cm⁻¹ (a) bitumen A, (b) bitumen B, (c) bitumen C and (d) bitumen D; solid lines KBr pellet spectra; dotted lines methylene chloride solution spectra

Table 7 Proton n.m.r. assignments for soluble fractions

Assignments ^a	Chemical shifts ^b (ppm)								
	Bitumen	Bitumen from sludge	Asphaltenes	Bitumen A	Bitumen B	Bitumen C	Bitumen D	Methanol extract	Methylene chloride extract
Terminal CH ₃ (0.5–1.0)	0.88 br	0.9 br	0.9 br	0.88 br	0.9 comp	0.93 br	0.85 br	0.87	0.9 br
Methyl β, Methylene β (1.0–2.0)	1.25 br	1.27 br	1.25 br	1.25	1.25 comp	1.25 br	1.27	1.23	1.25
Cyclic methylene (1.1–1.7)	—	—	—	—	—	—	1.73	—	1.8 br
Methyl α, (2.0–2.4)	2.23 br	2.25 br	2.2 br	2.2 comp	2.28 br	2.1 br	2.0	2.3 v.br	2.27 br
Methine, Methylene α (2.4–3.2)	2.5 v.br	2.7 v.br	2.7 v.br	2.5 v.br	—	2.6 v.br	—	—	—
Acetylinic (3.2–3.4)	—	—	—	—	—	—	—	—	—
Methylene Bridge (3.4–4.2)	—	—	—	3.55 w.br	3.55 br	3.67 br	3.63 br	3.6 br	3.67 br
Olefinic (4.2–5.8)	—	—	—	—	4.05 br	4.1	4.85 br	4.2 br	—
Monoaromatics (6.2–7.2)	7.0 v.br	7.1 br	7.2 v.br	7.1 v.br	7.1 v.br	7.25 v.br	7.1 comp, br	7.2 v.br	7.3 v.br
Polyaromatics (7.2–8.0)	7.0 v.br	7.65 v.br	7.2 v.br	7.1 v.br	7.1 v.br	7.25 br	7.6 br, 7.9 br	7.2 v.br	7.3 v.br
Phenolic, hydrogen bonded > 8.0	—	—	—	—	—	8.5 br	—	8.2	—
Width at half height of methylene resonance signal (1.0–1.4)	0.9	0.9	0.9	0.5	0.8	1.0	0.4	0.5	0.6

^a Ref. 34; ^b down field from tetramethylsilane; br = broad, comp = complex, w = weak

broadness of the peak suggests that both residual methanol and bridge methylene generally contribute to the intensity of the peak at ≈ 3.6 ppm.

Proton n.m.r. spectra of bitumens B, C and D appear to contain a broad and weak band at 4.1 ppm. This can be assigned either to the bridge methylene or olefinic protons. The presence of olefinic bonds is usually taken as evidence of a low level of thermal maturity of a sediment. Since the organic matter released from silicates is considered to be considerably older⁴⁴, the presence of olefinic bonds in this organic matter is difficult to explain. During the analyses of the light gases an increase in olefin production with exposure to air has been noted⁴⁴. Therefore, a possible explanation could be the production of olefinic bonds during exposure of organic matter to air in the tailings ponds.

The intensity and width at half height of the methylene signal (1.2–1.4 ppm) is said to be a measure of the methylene chain length⁴⁵. The longer the alkyl chain length, the greater the intensity and the narrower the width at half height of the signal. The values of the width at half heights of methylene signals are listed in Table 7. Alkyl chain length of bitumen B and C appears to be essentially similar to that of bitumen and asphaltenes. Bitumens A, D and methanol and methylene chloride extracts all appear to have comparable alkyl chain lengths that is about half that of the other fractions.

Greater broadening of the methylene signal in bitumens, asphaltenes, bitumen B and C can be ascribed to a higher degree of branching in these compounds⁴⁵. Shoulders on the downfield side of methylene resonance signal are assigned in part to the methylene hydrogens of branched alkanes⁴⁵, an assignment consistent with the above interpretation of the width of the methylene signal.

¹³C n.m.r. spectra

Soluble fractions from oil phase solids. ¹³C n.m.r. spectra of the soluble fractions from oil phase solids (OPS) were essentially similar. A typical spectrum of bitumen D is shown in Figure 9 together with the spectra of bitumen and asphaltene for comparison. The spectrum of the organics extracted from OPS appears to be quite complex compared with the spectra for bitumen and asphaltene.

The assignment of the short chain branch distribution in a low density polyethylene reported by Randall⁴⁶ can be applied to the peaks in the aliphatic region of the ¹³C n.m.r. spectra of the soluble fractions from oil phase solids. Following Linderman and Adams⁴⁷ and Dorman *et al.*⁴⁸, several peaks were assigned as shown in Table 8.

It is reasonable to assign the peak at ≈ 29.0 ppm to internal methylene carbons of longer paraffinic chains because the resonances of the corresponding terminal methyl and methylene are found at 12.7–14.0 (C¹), 22.4–22.8 (C²), and 30.4–31.8 (C³) ppm (see chemical formula) although α -methylene carbons of hydroaromatic may be found in the peak around 29 ppm.

The band between 15–18 ppm has been assigned to β -methyl in ethyl groups, although methyl groups, for example, in disubstituted hydroaromatic and naphthenic rings may also contribute⁴⁹. Based on this assignment the band at 16.8 ppm in the ¹³C n.m.r. spectra of bitumen D was assigned to the ethyl band, and the band at 20.8 is attributed to methyl α to an aromatic ring adjacent to one (e.g., 1-methynaphthalene) or no ring or group (e.g., 2-methynaphthalene).

Hydroaromatic substituents do not appear to be major

Figure 7 Proton n.m.r. spectra of soluble fractions from OPS (a) bitumen A, (b) bitumen B, (c) bitumen C, (d) bitumen D and (e) silylated kerogen D

structural types in the organic matter extracted from OPS. This conclusion is based on the fact that the ^{13}C n.m.r. spectrum of bitumen D has only a weak and broad band centred at 21.2 ppm which is in the region for hydroaromatics.

The region between 37–50 ppm contains resonances from bridgehead and other CH naphthenic carbons, some methylene bridge carbon (between sites, where one has no adjacent ring or group), alkyl CH other than in isoalkyl groups, and alkyl CH_2 adjacent to alkyl CH. Precise assignments in this region are difficult, but it appears that most of the above groups could be present in the organic matter extracted from OPS.

The region 50–100 ppm can be assigned to the O-alkyl carbon of alcohols, ethers and esters. All three fractions have small bands in the 50–60 ppm range usually assigned to methoxy or ethoxy carbons. Primary alcohols and ethoxy esters resonate over the range 60–65 ppm and a small amount of these materials may be present. The strong resonances in the 65–75 ppm range may be assigned to aryl alkyl ethers.

The spectra in the aromatic region are equally complex with a number of resonances spread over the range 110–175 ppm. The peaks in the range 169–173 ppm are assigned to the carbonyl resonance. The chemical shift range 148–168 ppm mainly contains resonances from aromatic carbons joined to hydroxyl and ether oxygen, while the range 100–115 ppm contain $\text{C}_{\text{ar}}\text{-H}$ ortho to these groups. The occurrence of resonances in both these regions indicates the presence of both phenolic and alkyl aryl ethers. The presence of alkyl aryl ethers is also supported by the resonances in the 60–75 ppm range. The presence of $\text{C}_{\text{ar}}\text{-C}$ resonances in 130–148 ppm range of the ^{13}C n.m.r. spectra indicate the presence of *peri*- and *cata*-condensed systems⁵⁰. The strong resonances in the 115–130 ppm range are assigned to $\text{C}_{\text{ar}}\text{-H}$ groups in soluble fractions from oil phase solids.

^{13}C n.m.r. spectra of insoluble fractions from oil phase solids. The CP/MAS ^{13}C n.m.r. spectra of the insoluble fractions from oil phase solids are shown in Figure 10

Figure 8 Proton n.m.r. spectra of solvent extracts from OPS (a) methanol extract, (b) methylene chloride extract

Figure 9 ^{13}C n.m.r. spectra of (a) bitumen from bituminous feedstock sand, (b) sludge pond bitumen, (c) asphaltenes and (d) bitumen D

Table 8 Assignment of ^{13}C n.m.r. spectra of soluble fractions from oil phase solids

Range of band from TMS	Assignment ^a
150–175	Phenolic carbon, aromatic ethers, carbonyl carbon
130–150	Aromatic carbon atoms substituted by alkyl groups and/or in condensed points
100–130	Unsubstituted aromatic carbon atoms (attached to hydrogen)
60–75	Aryl alkyl ethers
50–60	Methoxy or ethoxy carbon
8–50	Saturated carbon atoms
28–29.5	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--}(\text{CH}_2)_n\text{--CH}_2\text{--CH}_2\text{--}$
12.7–14.0	$\text{CH}_3\text{--}(\text{CH}_2)_n\text{--}$ $n > 3$
22.4–22.8	$\text{CH}_3\text{--CH}_2\text{--}(\text{CH}_2)_n\text{--}$ $n > 2$
30.4–31.8	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--}(\text{CH}_2)_n\text{--}$ $n > 2$
19.7 $\pm$ 0.3	$\text{--CH}_2\text{--CH--CH}_2\text{--}$
11.7 $\pm$ 1.0	$\text{CH}_3\text{--CH}_2\text{--}$

^a Refs. 47–50 and 53–56

along with the spectrum for unextractable organic matter associated with fines ($< 44 \mu\text{m}$ particles) from oil sands. The spectra of OPS, kerogen-D and oil sand fines all show the same general features. The assignments are listed in Table 9. The presence of a broad range of aliphatic

components is indicated by the resonance in the 0–50 ppm range. The major peak in this region is centred at 30 ppm, which is the chemical shift of methylene carbons in either long chain paraffinic structures or cycloparaffins. All three spectra show resonance in the 50–110 ppm region assigned to oxygen and nitrogen-substituted carbons as in carbohydrates, ethers, alcohols and amines (Table 9).

Figure 10 CP/MAS ^{13}C n.m.r. spectra of (a) oil sand fines (acid leached), (b) oil phase solids (acid leached), (c) kerogen-D and (d) methylated kerogen-D

Table 9 Assignment of ^{13}C chemical shift ranges

Chemical shift range ppm	Carbon type
0–50	aliphatic
50–110	aliphatic C–OH, C–OR, carbohydrate carbon
110–145	aromatic C–H aromatic C–C alkyl substituted aromatic
145–160	aromatic C–OH, C–OR
160–190	acid, ester, COOH, COOR
190–230	aldehyde, ketone

Region III, the 110–145 ppm region (Table 9), reflects aromatic and olefinic carbon resonances. Because no significant quantities of olefinic species have ever been detected in these materials, aromatic carbons are expected to be the major contributors to peaks in this region.

The region 145–160 ppm is characteristic of phenolic and aryl alkyl ether carbons, while carboxylic, amide and ester carbons are known to resonate in the 160–190 ppm region (Table 9). Although no distinct resolved peaks are observed in this region, the presence of some of these compounds is obvious from broad absorptions in these regions.

The CP/MAS ^{13}C n.m.r. spectrum of the methylated kerogen-D is shown in Figure 10d. A very strong peak for methoxy carbons at 55 ppm is indicative of the significant contributions from oxygen substituted carbons. The reversal of the intensity of the aliphatic and aromatic carbon signals is the most surprising feature of this spectrum compared with the spectrum of the untreated samples. The reason for this intensity reversal is not understood, although similar behaviour was observed for some methylated coal samples⁵¹.

The CP/MAS ^{13}C n.m.r. spectrum of a humic acid sample obtained from OPS after exhaustive extractions with 2% aqueous sodium hydroxide is shown in Figure 11c. The general features of the spectrum are similar to those of the OPS and kerogen-D spectrum. There is a broad resonance extending from 0 to 50 ppm indicative of aliphatic components. Oxygenated carbons, such as those in ethers, alcohols and carbohydrates does not appear to contribute significantly as apparent from the weak absorption in the 50–110 ppm region. The strong resonance, from 110–145 ppm and centred at ≈ 130 ppm, is due to protonated aromatic carbon, bridge head and alkyl-substituted carbon. The presence of phenolic and aryl alkyl species is indicated from the resonance in the region 145–160 ppm. A broad resonance in the 160–190 ppm region suggests significant contributions from acidic and ester components. A small resonance in the 190–220 ppm region could be due to the presence of aldehydes or ketones (Table 9).

In order to distinguish ^{13}C directly bonded to a hydrogen from carbons not directly bonded to hydrogens, a dipolar dephasing experiment²⁴ was carried out for this humic acid sample. The basis behind the experiment is that the transverse relaxation time of a ^{13}C directly bonded to a hydrogen, e.g., in aliphatic methylene or methine groups or an aromatic ring hydrogen on a perimeter aromatic ring carbon, is about 12 μs . The transverse relaxation time of carbons not directly bonded to hydrogens (e.g., quaternary aliphatic carbons, carboxyl and carbonyl carbons, and carbons in the interior of aromatic rings) is of the order of 200 μs . Carbons in methyl groups are a special case because of motion, and have T_2^* s of roughly 100 μs , under conditions of magic angle spinning. The differences in these T_2^* s in the absence of strong proton decoupling can be used to allow the carbons with shorter T_2^* to relax before starting proton decoupling and observation of carbons with larger T_2^* . The result is that with appropriate corrections for the decay of signals from the zero of time, the signals from the two different types of carbons may be separated. Figure 11(d,e) shows the result of such a dipolar dephasing experiment on the humic acid sample. The interpretation of the difference (11e) between

Figure 11 CP/MAS ^{13}C n.m.r. spectra of (a) peat humic acid, (b) humic acid from subbituminous coal, (c) humic acid from OPS, (c) as in c, with dipolar dephasing and (e) difference between c and d

the spectrum of the humic acid (11c) and that obtained using dipolar dephasing time of 40 μs (11d) is simple in this case. The dipolar dephased spectrum represents quaternary aliphatic carbons, phenolic, carboxyl and carbonyl carbons and carbons in the interior of the aromatic rings. The difference spectrum represents mostly methylene and methyne carbons in the aliphatic region and perimeter carbons in the aromatic region. The appearance of the resonance in the 190–220 ppm region in the dipolar dephased spectrum and its absence in the difference spectrum suggests the presence of ketones and the absence of aldehydes.

The CP/MAS ^{13}C n.m.r. spectra for a sample of peat humic acid and humic acid from a subbituminous coal are shown in Figures 11a and b, respectively. The peat humic acid sample is much less mature than the subbituminous coal humic acid samples, as evident from the stronger and sharper resonances due to the presence of carbohydrates, polysaccharides, phenols and

Table 10 Aromaticities (f_a) of bitumens, oil phase solids and the related materials

Sample	f_a	
	From proton n.m.r. ^a	From C-13 n.m.r.
Oil sand bitumen	0.31	0.31
Sludge pond bitumen	0.35	0.33
Asphaltenes	0.45	0.42
Maltenes	0.25	0.27
Bitumen-A	0.39	—
Bitumen-B	0.39	—
Bitumen-C	0.36	0.38
Bitumen-D	0.44	—
OPS	—	0.54
Unextractable organic matter from oil sands ^b	—	0.53
Kerogen-D	—	0.53
Soil humic acids	—	0.31
Humic acid from subbituminous coal	—	0.49
Humic acid from OPS	—	0.50

^a Brown and Ladner's method; reference 52^b Associated with $\leq 44 \mu\text{m}$ particles in oil sand

carboxylates. Comparing all three spectra, there appears to be a resemblance between the spectra of humic acid from OPS and that of subbituminous coal. This suggests that humic acid from oil phase solids and subsequently the oil sands are of comparable maturity to that of subbituminous coal. The possible effect of degradation during hot water processing and subsequent tailings pond storage is of course unknown.

Aromaticities (f_a), defined as the ratio of the aromatic carbon to total carbon, were determined directly from the ^{13}C n.m.r. spectra and from proton n.m.r. spectra using Brown and Ladner's method⁵². Table 10 lists the values of f_a determined by both methods. There is a reasonable agreement between the two sets of values. It is evident from the table that at least 1/3 of the total carbons in these fractions are in aromatic locations. Kerogen-D, humic acid and unextractable organic matter associated with clay in oil sands all have higher aromaticities than the soluble organic matter. Also the aromaticities of insoluble fractions is comparable to the corresponding value for humic acids from subbituminous coals. This again suggests the humic matter associated with oil sands is of comparable maturity to that of subbituminous coal.

The chemical extraction technique proved to dissociate most of the mineral constituents, successfully thus decreasing considerably the ash content of the insoluble organic matter and making it more amenable to spectroscopic study. Infrared and n.m.r. spectroscopic results clearly demonstrate the presence of such compounds as hydrogen bonded phenols, alcohols, ethers, amides, polyaromatics with long paraffinic chains, carboxylic acids, quinones and ketones. This is consistent with the elemental composition of this organic matter which is indicative of the material being humic. Most of the above compounds are capable of forming chemical bonds with metals, and metal oxides. Chemical bonding between phenols, ethers, amides, carboxylic acids, quinones and ketones and metals appears quite probable. However, physisorption of longchain and branched paraffins would seem to be more likely than the formation of chemical bonds, although hydrogen bonding and other similar covalent or ionic interactions cannot be disregarded. Similarly, the presence of substantial

concentrations of esters in the organic matter associated with oil phase solids suggests strongly bonded ester silicate complex, but physisorption may also be occurring.

It is obvious from the foregoing results that the humic material associated with heavy metal minerals is different from bitumen and bitumen components. It appears to be of comparable maturity to that of humic acids from subbituminous coals. It must be borne in mind, however, that the material isolated has been through the hot water process and stored in the tailings pond, so that considerable alteration may have taken place. It is difficult to draw any conclusions regarding the geochemical nature of this material with respect to the origin and maturity of bitumen. However, comparisons of this organic matter with the unextractable organic matter associated with clay from oil sands might be more useful to answer some of the questions in this respect. Further work is in progress.

CONCLUSIONS

The insoluble organic matter associated with oil-wet minerals in Suncor aqueous sludge was isolated in combined dissolution-extraction techniques. A number of soluble products were obtained as well as a base-soluble humic acid fraction and a kerogen concentrate. The oxygen and sulphur content of these fractions is considerable, representing many types of functional groups. Composition and n.m.r. studies suggest that the humic acid and kerogen fractions resemble those obtained from humic coals of lignite or subbituminous rank.

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